

PATENT ABSTRACTS OF JAPAN

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(54) PRODUCTION OF POWDER PARTICLE

(57)Abstract:

PURPOSE: To obtain composite particles useful as an antistatic agent for a resin, rubber, etc., through an extremely simple procedure by spray-drying a mixture of an emulsion of a polymer having a specific glass transition temp. with a fine metal (compound) powder having a specific average particle diameter.

CONSTITUTION: 100 pts.wt. (on solid basis) emulsion of a polymer having a glass transition temp. of -40°C or higher is mixed with 1-300 pts.wt. powder of a metal or metal compound having an average particle diameter of 50µm or smaller. The mixture is spray-dried to produce powder particles. By thus incorporating spray drying into an emulsion polymerization process, the objective method is far simpler than the conventional methods. The metal to be mixed with the emulsion can be used in any amount. The particles are useful as an antistatic agent for a resin, rubber, etc., and are applicable to a coating composition, sealant, electromagnetic wave shield, magnetic tape, etc. The particles can also be used in combination with any of various active ingredients, such as a drug, dye, detergent, etc., to produce a composite material.

LEGAL STATUS

[Date of request for examination]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacture approach of the powder particle of a polymer and a metal.

[0002]

[Description of the Prior Art] Organic-inorganic complex particle is used for resin, the antistatic agent of rubber, a toner, and various electric weight components ingredients as an ingredient which combines which cheap property in the goodness of the compatibility of properties, such as metaled conductivity and magnetism, and the light weight of an organic substance and resin, and the ease of processing it. Conventionally, the following approach is learned as the manufacture approach of organic-inorganic complex particle. (I) How to make oil solubility or a water-soluble monomer distribute a metal powder, add the monomer (oil solubility water solubility and water solubility oil solubility) of the property to be behind reverse, and carry out an interfacial polymerization on a particle front face.

(II) How to gel a particle front face and solidify by change of pH of a medium, electrolytic addition, addition of a dehydration solvent, a temperature change, etc., after making the oil solubility matter distribute a metal powder and adding hydrophilic sol matter, such as polyvinyl, alcohol, gum arabic, methyl cellulose, ethyl cellulose, gelatin, and protein, behind.

(III) How to make metal fine particles collide with an organic substance particle by the high-speed flow.

[0003]

[Problem(s) to be Solved by the Invention] By said conventional manufacture approach, it needed a complicated process and actuation, and the approach of manufacturing organic-inorganic complex particle had low productive efficiency, and was a disadvantageous approach industrially. Moreover, the approach of blending many amounts of the metal which can be compounded was difficult. Therefore, when the conventional composite particle was used as an antistatic agent of resin, the expectable engine performance was very low. The purpose of this invention is to offer the new manufacture approach that the complex particle which has the antistatic effectiveness which was excellent in the Plastic solid can be obtained with high productive efficiency according to a simple process.

[0004]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, as for this invention, glass transition temperature offers the approach of carrying out spray drying of the mixture with which mean particle diameter mixed a metal 50 micrometers or less or metallic compounds 1 - the 300 weight sections, and manufacturing a powder particle, to a polymer emulsion (solid content 100 weight section) -40 degrees C or more. The polymer emulsion in this invention can be conventionally manufactured by the well-known emulsion-polymerization approach. That is, it is obtained by adding a monomer and a polymerization initiator, an emulsifier, a polymerization chain transfer agent, etc. to an aquosity medium (usually water), and performing an emulsion polymerization.

[0005] The monomer used for manufacture of the aquosity dispersing element of this invention It is chosen from the monomer in which a radical polymerization is possible. A butadiene, an isoprene,

Conjugated diene system compounds, such as 2-Krol-1,3-butadiene and 2-methyl-1,3-butadiene; Styrene, Aromatic series vinyl compounds, such as alpha methyl styrene, vinyltoluene, and p-methyl styrene; A methyl acrylate, An ethyl acrylate, butyl acrylate, acrylic-acid 2-hydroxyethyl, The alkyl ester compound of acrylic acids, such as methacrylic-acid 2-hydroxyethyl and methacrylic-acid GURIJIRU, or a methacrylic acid; Acrylamide, Carboxylic-acid vinyl ester, such as acrylamide of ethylene system unsaturated carboxylic acid, such as methacrylamide, N,N-dimethylacrylamide, and N-methylol acrylamide, or methacrylamide compound; vinyl acetate; Acrylonitrile, a methacrylonitrile, Vinylcyanide compounds, such as alpha-KURORU acrylonitrile; An acrylic acid, Monocarboxylic acid, such as a methacrylic acid and a crotonic acid; A maleic acid, a fumaric acid, Dicarboxylic acid, such as an itaconic acid; the ethylene system partial saturation monomer of unsaturated carboxylic acid, such as half ester, such as maleic-acid methyl, itaconic-acid methyl, and beta-METAAKURIRUOKISHIECHIRUASHIDDO hexa hydro phthalate, etc. can be mentioned further. These can also be used combining two or more sorts, even if independent. Among these monomers, the following combination is desirable.

[0006] (1) it consists of a conjugated diene system compound and other copolymerizable monomers, and both weight ratios are 1-45/55 -- put together. [99-55]

(2) the carbon number of an alkyl group consists of an acrylic ester (meta) compound of 4-12, and other copolymerizable monomers, and both weight ratios are 15-75/25 -- put together. [85-25]

(3) the carbon number of a conjugated diene system compound and an alkyl group consists of an acrylic ester (meta) compound of 4-12, and other copolymerizable monomers, and both weight ratios are 1-60/40 -- put together. [99-40]

In addition, the above (1) - (3) With other copolymerizable monomers which can be set, dicarboxylic acid, such as monocarboxylic acid, such as vinylcyanide compounds, such as aromatic series vinyl compounds, such as styrene, alpha methyl styrene, vinyltoluene, and P-methyl styrene, acrylonitrile, a methacrylonitrile, and alpha-KURORU acrylonitrile, an acrylic acid, a methacrylic acid, and a crotonic acid, a maleic acid, a fumaric acid, and an itaconic acid, etc. is mentioned, and two or more sorts of these can be used. -40 degrees C or more of 0 degrees C or more of the glass transition temperature of the polymer of this invention are 30 degrees C or more more preferably. When spray drying is carried out to this glass transition temperature being less than -40 degrees C, even if a particle is not obtained or it is obtained, it becomes the particle to which welding happens remarkably.

[0007] There is especially no limit about the polymerization initiator used for the emulsion polymerization in this invention, for example, inorganic system polymerization initiators, such as persulfate, such as organic system polymerization initiators, such as azo compounds, such as peroxide, such as hydroperoxide, such as a cumene hydroperoxide, diisopropylbenzene hydroperoxide, and paramenthane hydroperoxide, benzoyl peroxide, and lauroyl peroxide, and azobisisobutyronitril, and potassium persulfate, sodium persulfate, and ammonium persulfate, can be used. In addition, the above-mentioned polymerization initiator can be used also as the so-called redox system polymerization initiator combined with reducing agents, such as sodium bisulfite.

[0008] There is especially no limit about the emulsifier used for the emulsion polymerization in this invention, and both an anion mold the Nonion mold and a both-sexes mold surfactant can be used. These can also be used as two or more sort mixing, even if independent. For example, the Nonion mold surface active agents, such as anion mold surface active agents, such as a sulfonate of aliphatic series carboxylate, such as alkylbenzene sulfonates, such as a sulfate salt of higher alcohol, such as sodium lauryl sulfate, and sodium dodecylbenzenesulfonate, and sodium dioctyl sulfosuccinate, an alkyl ester mold of a polyethylene glycol, an alkylphenyl ether mold, and an alkyl ether mold, etc. can be used.

[0009] Moreover, as an amphoteric surface active agent, what has carboxylate, a sulfate salt, a sulfonate, a phosphoric acid salt, and a phosphoric ester salt as an anion part, and has an amine salt and quarternary ammonium salt as a cation part can be mentioned. Specifically, the salt of a lauryl betaine, a stearyl betaine, a cocamidopropyl betaine, and 2-undecyl hydroxyethyl imidazolium betaine can mention the salt of the lauryl-beta-alanine, the stearyl-beta-alanine, a RAURIRUJI (aminoethyl) glycine, an OKUCHIRUJI (aminoethyl) glycine, and a JIOKUCHIRUJI (aminoethyl) glycine as an amino acid type

thing as a salt of an alkyl betaine again. These can also be used combining two or more sorts, even if independent.

[0010] There is especially no limit about the polymerization chain transfer agent used for the emulsion polymerization in this invention. An alpha-methyl-styrene dimer, the alpha-methyl-styrene dimer which contains a 2-4-diphenyl-4-methyl-1-pentene component 60% of the weight or more preferably, TAPINOREN, alpha-terpinene, gamma-terpinene, a dipentene, an octyl mercaptan, n-dodecyl mercaptan, t-dodecyl mercaptan, n-hexadecyl mercaptan, Diethyl xantho gene disulfide, dimethyl xantho gene disulfide, Diisopropyl xantho gene disulfide, tetramethylthiurammonosulfide, A tetraethylthiuram disulfide, tetrabutylthiuram disulfide, JIPENTA methylene thiuram disulfide, etc. can be used, and these can also be used combining two or more sorts, even if independent.

[0011] There is especially no limit about the emulsion-polymerization approach in this invention, and its condition, and it can carry out under a well-known approach and a condition conventionally. For example, any of the methods which emulsify beforehand a package addition method, a division addition method, a continuation addition method, and a monomer about the addition approach of a monomer, and are added, or such combination are sufficient. From points, such as reduction of generation of a congelation, and removal of heat of reaction, a division addition method, a continuation addition method, or the emulsified continuation addition method of a monomer is desirable among these methods. The polymer emulsion obtained contains a 0.05-0.5-micrometer particle-like polymer preferably the particle diameter of about 0.01-2 micrometers. The solid content of this polymer emulsion is usually 20 - 50 % of the weight preferably ten to 65% of the weight, and viscosity is 1-30,000cps preferably. Since trouble may be caused to spray drying if this solid content is smaller than 10 % of the weight, it is not desirable.

[0012] For example, a metal simple substance, a metallic oxide, a metal hydroxide, etc. are mentioned, and, as for the metal in this invention, zinc, nickel, iron, and antimony are preferably mentioned, for example for copper, tin, zinc, nickel, iron, aluminum, silver, gold, platinum, antimony, palladium, chromium, cobalt, a tungsten, an yttrium, etc. as a metal component. These can also be used independently, and even if they use for coincidence about plurality, they do not interfere. Moreover, you may use in the form of an alloy. As for a metal, it is desirable that they are fine particles, and a configuration has a globular form, linearity, a monotonous form, etc.

[0013] the polymer emulsion (solid content) 100 weight section from which the complex particle in this invention was obtained by the above-mentioned approach -- receiving -- a metal or metallic compounds 1 - the 300 weight sections -- they are the 5 - 200 weight section and the thing which carries out 10-100 weight section mixing still more preferably, and is obtained by carrying out spray drying preferably. When the effectiveness which a metal or metallic compounds has as the amount of a metal or the metallic compounds used is under 1 weight section is not acquired and it uses for an antistatic application, for example, the effectiveness is not fully acquired. Moreover, if the 300 weight sections are exceeded, a metal or metallic compounds is superfluous, mixing with a polymer emulsion is difficult and compound-izing of a metal and a polymer is also difficult mixing. In the case of spray drying, ***** arises in an atomiser and that to which the mean particle diameter of a metal or metallic compounds exceeds 50 micrometers is difficult disintegration. Moreover, 50 micrometers or less of mean particle diameter of a metal or metallic compounds are 10 micrometers or less preferably. Here, as for mean particle diameter, in a globular form case, the thing of linearity or a monotonous form shows the greatest die length for the diameter. Moreover, mean particle diameter is the average of the particle size of 500 particles observed and obtained with the electron microscope.

[0014] 50-180 degrees C of spray drying are more preferably performed by equipments, such as for example, a rotating-disc mold atomizer, a pressure nozzle mold atomizer, and a two fluid nozzle mold atomizer, under the temperature of 100-140 degrees C. The polymer emulsion which carries out spray drying may be independent, and may be the mixture of two or more polymer emulsions. However, when two or more polymer emulsions are mixed, the glass transition temperature when carrying out the weighted mean of each polymer needs to be -40 degrees C or more. In order to prevent the blocking at the time of spray drying and to raise neglect stability etc. further, spray drying of minerals bulking

agents, such as clay which is a well-known anti-binder, talc, a silica, diatomaceous earth, or a calcium carbonate, polyvinyl alcohol, polyacrylamide, etc. can also be added and carried out if needed. The mean particle diameter of the powder particle of this invention is usually 5-100 micrometers. In spray drying, conditions, such as properties, such as a presentation of a polymer emulsion, particle diameter, and glass transition temperature, the rate of mixing of an aqueous dispersing element, total solids and the added class of anti-binder, a rate, a class of atomiser, inlet temperature, outlet temperature, and airflow, are chosen suitably. The powder particle obtained by this invention is useful to antistatic agents, such as resin and rubber, and can be applied to a toner, a coating, a floor polish, encapsulant, an electromagnetic wave shielding agent, a magnetic tape, etc.

[0015]

[Example] Next, although an example explains this invention to a detail further, thereby, this invention is not restricted. In addition, in the following publications, "%" and the "section" express weight % and the weight section.

(1) The manufacture approach of the polymer emulsion the monomer presentation shown in the manufacture table 1 of a-c of a polymer emulsion is as being shown below. In addition to the monomer component shown in Table 1, as a chain transfer agent, it taught the sodium dodecylbenzenesulfonate 0.5 section as the t-dodecyl mercaptan 0.3 section and an emulsifier, and the potassium persulfate 0.5 section and the water 150 section were taught to the autoclave made from stainless steel of 100l. of content volume as a polymerization initiator, the emulsion polymerization was carried out, agitating at the polymerization temperature of 50-80 degrees C under nitrogen-gas-atmosphere mind, and the polymer emulsion was manufactured. The polymerization invert ratio was 99%.

[0016]

[Table 1]

| 重合体エマルジョン | a | b | c |
|--------------|-----|-----|-----|
| 単量体組成 | | | |
| ブタジエン | 33 | — | 70 |
| ブチルアクリレート | — | 24 | — |
| スチレン | 31 | 10 | 20 |
| メチルメタアクリレート | 19 | 46 | — |
| アクリロニトリル | 13 | 10 | 10 |
| アクリル酸 | 4 | 10 | — |
| ガラス転移温度 (°C) | +10 | +70 | -60 |

[0017] (2) Manufacture of a complex particle (1) Spray drying of obtained polymer emulsion a-c was carried out to the metal powder shown in Table 2 with the combination of examples 1-3 and the examples 2-5 of a comparison. Spray drying of the example 1 of a comparison is carried out without including a metal powder at all. Spray drying was performed using the two fluid nozzle of product [made from EYELA], and SD-1 desk spray dry on conditions with an inlet temperature [of 80-120 degrees C], and an exhaust air temperature of 45-80 degrees C. Compound-ization of each example was evaluated and the result was shown in Table 2. The evaluation approach observed the obtained powder with the reflective mold analytical electron microscope, performed metal elemental analysis about the fine-particles particle, and performed it whether the metal is contained in fine particles, and by analyzing.

○ Mark : the metal powder is compounded.

x mark: The metal powder is not compounded.

Furthermore, about what the metal compound-ized to the polymer, it asked for the weight ratio of a polymer/metal by thermogravimetric analysis.

[0018]

[Table 2]

| | 実 施 例 | | | 比 較 例 | | |
|---------------------|--------|--------|--------|-------|-------|-------|
| | 1 | 2 | 3 | 1 | 2 | 3 |
| 重合体エマルジョンの種類 | a | b | a | a | b | c |
| | 1 0 0 | 1 0 0 | 1 0 0 | 1 0 0 | 1 0 0 | 1 0 0 |
| 金属粉 亜鉛 (5 μ m) | 4 0 | — | 2 0 | — | — | 5 0 |
| ニッケル (3 μ m) | — | 6 0 | 3 0 | — | 3 2 0 | — |
| ニッケル (6 0 μ m) | — | — | — | 5 0 | — | — |
| 複 合 化 | ○ | ○ | ○ | × | × | — |
| 平 均 粒 径 (μ m) | 6 2 | 5 8 | 7 0 | 6 5 | 5 5 | — |
| 重合体／金属比 (重量) | 100/37 | 100/58 | 100/48 | — | — | — |

[0019] the composite particle which examples 1-3 are the complex powder obtained within the limits of this invention, and is made into the purpose of this invention -- profit *****. This invention of the metal powder used for compound-ization was out of range at 60 micrometers, and on the occasion of spray drying, ***** arose for the nozzle of spray dry, and the example 1 of a comparison was bad in powdered production, and was not enough for it. [of compound-izing] The metal powder of this invention which used the example 2 of a comparison for compound-ization was out of range in the 320 sections, the metal powder was superfluous on the occasion of spray drying, the obtained fine particles were not compound-ized but the mixture of a metal powder and an organic substance was obtained. The glass transition temperature of this invention of a polymer emulsion is out of range at -60 degrees C, and adhered to the generating tube of spray dry in the case of spray drying, and, as for the example 3 of a comparison, a composite particle was not able to be obtained.

[0020]

[Effect of the Invention] According to the manufacture approach of this invention, as compared with the approach of manufacturing the conventional complex particle, a complex particle can be manufactured by the remarkable simple approach by adopting an emulsion-polymerization process spray drying means. And this complex particle can adjust the amount of the metal to compound freely, for example, is useful to antistatic agents, such as resin and rubber, and can be applied to a toner, a coating, a floor polish, encapsulant, an electromagnetic wave shielding agent, a magnetic tape, etc. Moreover, a compound-ized technique is used, and by spraying active principles, such as perfume, physis, agricultural chemicals, a color, a detergent, fats and oils, food, an enzyme, liquid crystal, a rust-proofer, a catalyst, a flame retarder, and an antioxidant, on coincidence at the time of spray drying, -izing can be carried out [****] and it can use for various applications, such as drugs and cosmetics, according to the active principle contained inside.

[Translation done.]